

## Transfer Printing of Colloidal crystals based on UV mediated degradation of a polymer thin film

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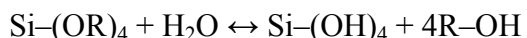
### Online Supporting Information

#### *S1.0 Colloids used:*

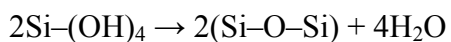
1. **PS colloids:** Monodispersed colloids of polystyrene (PS) having diameter  $d_p = 100, 300, 600$  and  $800$  nm were purchased from Sigma, UK. They were further diluted in methanol for spin coating.
2. **Silica colloids:** Monodisperse silica particles of diameter ( $d_p$ )  $350$  nm were synthesized following Stöber's method by hydrolysis of tetraethyl orthosilicate (TEOS) (99.99%, Sigma-Aldrich) in ethanol (99.99%, Sigma-Aldrich) medium in the presence of ammonium hydroxide (28%, Sigma-Aldrich) as a catalyst.<sup>1,2</sup>

During the synthesis process two main reactions are involved:

- (i) Formation of silanol group by hydrolysis



- (ii) Formation of siloxane bridges by condensation polymerization reactions



Ethanol was first taken in a beaker and kept in a sonication bath, to which a pre-calculated amount of TEOS was added. After 20 minutes of sonication, 28% ammonium hydroxide was added as a catalyst to promote the condensation reaction. Sonication was continued for another 60 min to get a white turbid suspension. All the steps were conducted at room temperature. The silica suspension was allowed to stand for an hour

and then dried and calcined to obtain silica powder. The silica powder was re-dispersed in ethanol prior to spin coating.

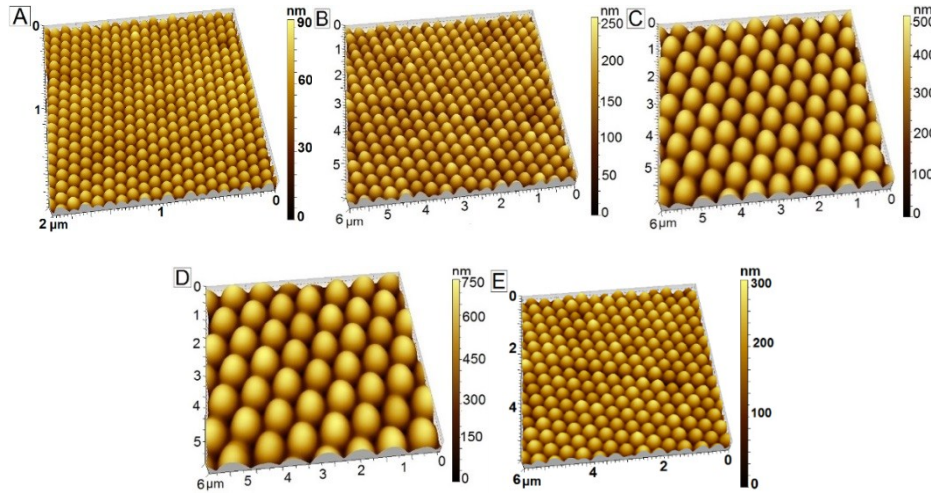
### ***S2.0 Base substrate or stamp preparation***

First, the spin coated colloidal arrays were created on the base substrate or stamp which comprises of a thin Poly(methyl methacrylate) (PMMA, Molecular weight: 120 K, Sigma Aldrich, USA) film coated on a self-standing block of crosslinked Sylgard 184 (a thermocurable PDMS based elastomer, Dow Corning, USA). The degassed mixture of oligomer and crosslinker (ratio maintained at 10:1) was poured in a glass mould, with variable spacer length for controlling the final block thickness, and thermally annealed at 120 °C for 12 hours. The thickness of the Sylgard blocks were kept constant at  $\approx 500\ \mu\text{m}$  in our experiments. These self-standing square blocks (15 mm x 15 mm) were stuck on solid glass substrate with double sided tape, prior to spin coating of PMMA on it.

Films of PMMA were spin cast from a dilute solution in toluene (dilution: 1 wt%, drop volume: 200  $\mu\text{L}$ , RPM: 2500, spin duration: 1 minute) onto these Sylgard blocks. The PMMA film thickness was maintained  $\approx 40\ \text{nm}$ . Film thickness was verified using an Ellipsometer. In cases, the PMMA film was patterned for obtaining the non close packed arrays, the initial PMMA film thickness was maintained  $\approx 140\ \text{nm}$ . The PMMA films were patterned following pressure assisted capillary force lithography, using patterned flexible foils as stamps for using as substrates.<sup>3,4</sup> The thickness of the remnant PMMA layer within the patterned grooves was maintained  $\approx 40\ \text{nm}$ .

### ***S3.0 Creation of colloidal arrays by spin coating on flat and patterned PMMA films***

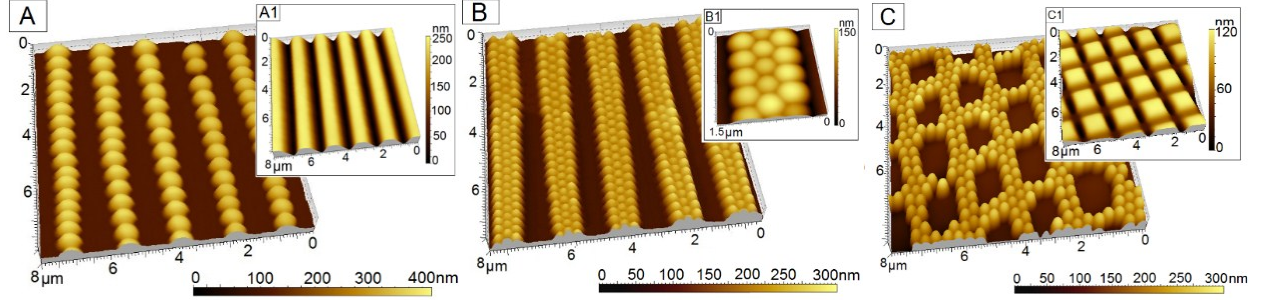
PS colloids with  $d_p = 100, 300, 600$  and  $800$  nm and synthesized silica colloids of  $d_p = 350$  nm were spin coated from diluted solutions in methanol and ethanol respectively on the flat and patterned PMMA substrates. Small amount of sodium dodecyl sulfate (SDS) was added in both the cases to stabilize the colloidal sol. Ahead of spin coating, dilute solutions of PS colloids in methanol and silica colloids in ethanol was mixed with dilute solution of SDS in the respective solvents and was sonicated in a water bath for 1 hour. Subsequently,  $100 \mu\text{L}$  of the stabilized colloidal sol was spin coated on the PMMA substrates. The duration of spinning was 5 minutes in each case. Fig. S1 shows the AFM images of the hexagonal close packed (HCP) arrays formed on flat PMMA films.



**Fig. S1** As cast morphology of the self assembled HCP array of colloidal particles on thin PMMA films. (A) PS colloids, particle diameter  $d_p = 100$  nm; (B) PS colloids,  $d_p = 300$  nm; (C) PS colloids,  $d_p = 600$  nm; (D) PS colloids,  $d_p = 800$  nm and (E) Silica colloids,  $d_p = 350$  nm.

Spin coated non close packed (NCP) arrays were fabricated on the topographically patterned substrates. On a topographically patterned substrate, the evaporating film during late stage of spin coating ruptures along the contours of the pattern walls, thereby confining the colloids within the substrate grooves.<sup>7</sup> The final morphology is strongly influenced by a combination of

evaporation induced capillary forces and centripetal forces under physical confinement.<sup>5,6</sup> The relative commensuration between the size of the colloids and the feature geometry also plays an important role. Fig. S2 shows the AFM images of colloids coated on grating patterned PMMA films.



**Fig. S2** Spin coated morphology of colloids on the patterned templates. The details are: (A)  $d_p = 600$  nm, ordered using Template 1 with  $l_p = 750$  nm. Inset A1 shows morphology of Template 1. (B)  $d_p = 300$  nm on Template 1. Inset B1 shows a magnified AFM image of the zig-zag nature of the array. (C)  $d_p = 300$  nm, 2D colloid array on Template 2 comprising square pillars as shown in inset C1.

Template 1 has a grating geometry with periodicity  $\lambda_p = 1.5$   $\mu\text{m}$  and line width ( $l_p$ ) = 750 nm (shown in the inset of Fig. S2A). The second template (Template 2) comprises of array of square pillars (750 nm x 750 nm) placed at a periodicity of  $\lambda_p = 1.5$   $\mu\text{m}$  in both X and Y directions (inset of Fig. S2C). Fig. S2A and S2B shows the particle assembly when PS colloids with diameter  $d_p = 600$  nm and  $d_p = 300$  nm are spin coated on Template 1. The arrangement in Fig. S2A was obtained for  $C_n = 0.8$  wt% and RPM = 2500. In contrast, the optimized condition for obtaining the structure shown in Fig. S2B was  $C_n = 0.4$  wt% and RPM = 2500. Due to near perfect commensuration between  $d_p = 600$  nm and  $l_p = 750$  nm, single thread of colloids was obtained along every substrate groove in Fig. S2A. On the other hand, a zig-zag arrangement of the colloids with local HCP symmetry along the substrate grooves was observed in Fig. S2B, as  $l_p$  (750 nm) is exactly 2.5 times of  $d_p$  (300 nm).

#### ***S4.0 Characterization:***

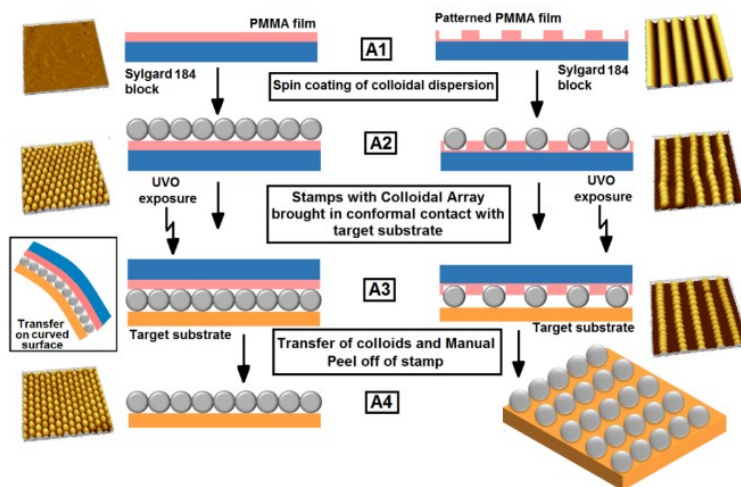
The morphology of the as-cast colloidal arrays and the arrays after transfer printing on different surfaces was investigated using a Field Emission Scanning Electron Microscope (FESEM) (JSM7610F, JEOL, Japan) and an AFM (Agilent Technologies, AFM 5100) in intermittent contact mode using a silicon nitride cantilever (PPP-NCL, Nanosensors Inc., USA). Interestingly, we could scan the array transferred on to the curved surface of the test tube as well, using the AFM (Figure 3B). This was possible as the sample plate in the particular model of AFM we used is free from any electronics. We used a specially designed sample plate with a large opening in the middle and the test tube containing the transferred array was attached to the bottom of the plate. The region of interest could be accessed by the AFM tip through the opening in the sample plate.<sup>3</sup>

X-ray Photoelectron Spectroscopy (XPS) of the samples was conducted by means of a PHI 5000 Versaprobe-II spectrometer using a monochromatic Al source at 1486.6 eV photon energy. The optical characterization of the samples was performed by recording the transmission and reflectance spectra using UV-Vis-NIR spectrophotometer (Avantes Spectrometer, Starline and NIRline). The details of materials and methods adopted are described in the following sub sections.

#### ***S5.0 Transfer Printing of colloids: The Procedure***

The PMMA film coated with the colloids was brought in conformal contact with the target substrate (step A3, Fig. S3) and subject to UV exposure for 30 min in a UVO (PSD Pro UV-O, Novascan, USA) chamber. The samples were placed at a distance of 5mm from the UV lamp, with an average power output of 30 mW/cm<sup>2</sup>. As discussed in the main text, the PMMA film degrades with time due to UV exposure. Consequently, the

particles lose adhesion to the initial base substrate and transfer on to the target substrate. The steps involved are schematically shown in figure S3.

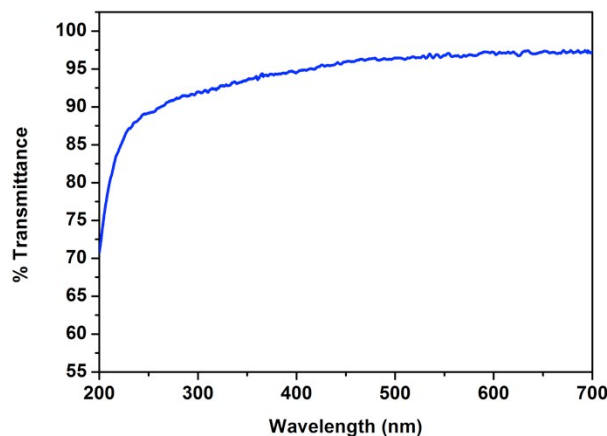


**Fig. S3** Schematic of Colloidal Transfer Printing based on UV mediated degradation of a sacrificial PMMA thin film.

As already mentioned in the text, different target substrates such as silicon wafer (surface energy,  $\gamma_s = 75 \text{ mJ/m}^2$ ) and silanized silicon wafer ( $\gamma_s = 25.4 \text{ mJ/m}^2$ ) were used to demonstrate that the proposed method can be used to transfer the array on to both hydrophilic and hydrophobic surfaces. Silanization of the silicon wafer were done by creating a self-assembled monolayer of octadecyltrichlorosilane (OTS, 95% pure, Aldrich, UK).

For transferring the array to a curved surface, a thinner Sylgard 184 support layer (thickness  $\approx 200 \text{ }\mu\text{m}$ ) was used to facilitate complete conformal contact.

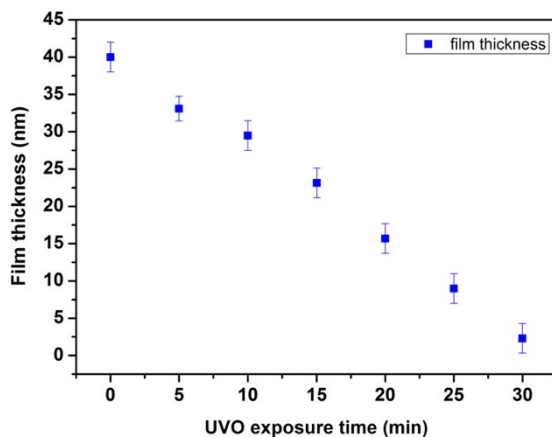
### ***S6.0 Transmittance spectra of Sylgard 184***



**Fig. S4** *Transmittance spectra of Sylgard 184 substrate exposed to UVO for a duration of 30 min.*

The transmittance spectra of a 500  $\mu\text{m}$  thick block of Sylgard 184 exposed to UV irradiation for 30 min is shown in Fig. S4. The film remains  $\sim 89.4\%$  transparent at the wavelength of 254 nm. This highlights that even though the surface of Sylgard 184 may undergo oxidation upon UV-Ozone treatment, its bulk transparency in the UV region does not change much within 30 min of UV exposure.<sup>7</sup> High transparency of the PDMS (Sylgard 184) block ensures that adequate amount of UV light reaches the PMMA film and leads to its degradation with time.

### ***S7.0 Rate of degradation of PMMA with UV exposure***

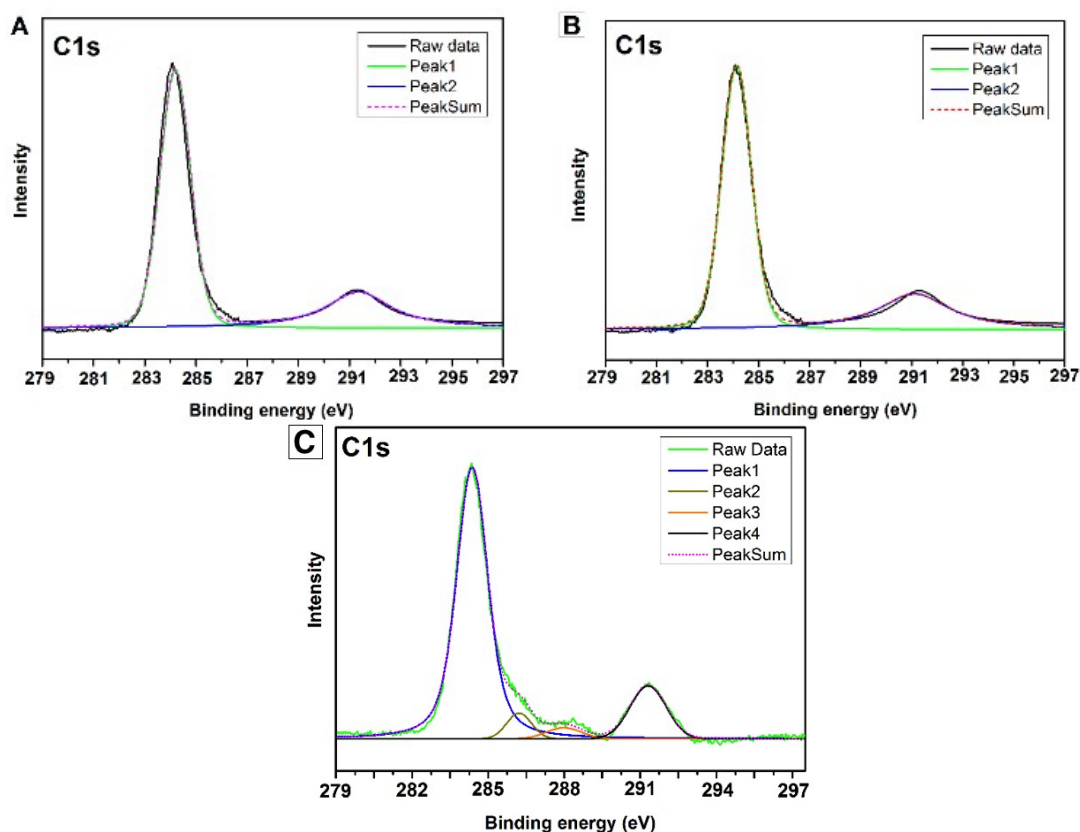


**Fig. S5** *Variation of PMMA film thickness with UV exposure time on Sylgard 184 substrate.*

It is mentioned in the main text that the PMMA film gradually degrades with time due to UV exposure. The rate of degradation of PMMA was determined with the help of an

Ellipsometer (Accurion, EP3 SW), where the change in thickness of PMMA film on Sylgard 184 substrate, placed upside down on a silicon wafer surface, was measured after different UV exposure time. The initial film thickness was 40 nm. The plot in Fig. S5 shows that a 40 nm thick PMMA film degrades at an almost uniform rate of 1.3 nm per minute. The film thickness reduces to  $\approx 2.3$  nm after 30 minutes of UV exposure.

### S8.0 X-ray Photoelectron Spectroscopy (XPS) analysis of Transferred Colloids



**Fig. S6** XPS spectra of C1s peak (raw and fitted curves) with deconvolution, for PS HCP array with  $d_p = 600$  nm: (A) Spin coated on the substrate; (B) Transferred on to silicon wafer with 30 min UV exposure; (C) Transferred on to silicon wafer with 60 min of UV exposure. The C1s peak has been deconvoluted by the Voigt function.

The XPS data for spin coated and transferred HCP array of PS colloids is shown in Fig. S6A and S6B respectively. The deconvoluted C1s spectra of spin coated PS colloids show presence of two distinct peaks at 284.5 and 291.3 eV which can be assigned to C–C/C–H and  $\pi$ – $\pi^*$  satellite peak respectively. The C1s spectra for transferred PS colloids on silicon wafer show exactly similar

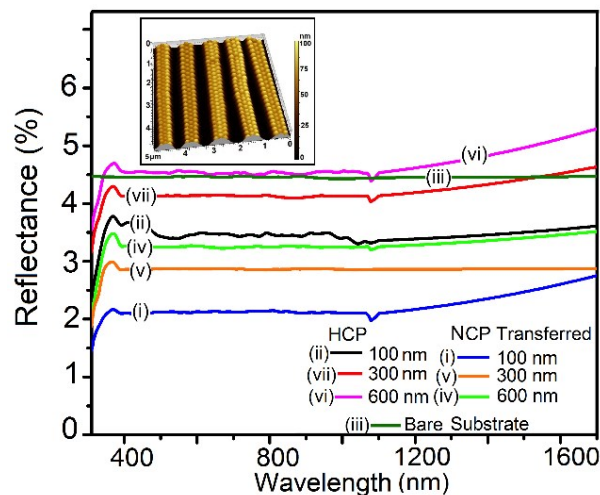


result with two distinct peaks at 284.5 and 291.3 eV. No peaks related to PMMA (that is C-O and C=O) were found in the deconvoluted C1s spectra of transferred PS colloids (Fig. S6B), thus confirming the absence of a PMMA layer on top of the transferred PS colloids.

XPS was also utilized to analyze the change in surface property of PS colloids with excess UV exposure during transfer. The UV exposure time was determined from the initial thickness of the PMMA film on the Sylgard 184 substrate. A 40 nm film takes 30 min to degrade and facilitate the transfer process. Over exposure would lead to degradation of the colloidal particles, post degradation of the sacrificial PMMA layer, as is evident from the XPS data shown in Fig. S6C. At long UV exposure time (60 min), the formation of new oxygen functional groups was observed.<sup>8</sup> The deconvoluted C1s high resolution spectra show presence of four peaks: a main C-C/C-H peak at 284.5 eV, C-O peak at 286.2 eV, carbonyl C=O peak at 288 eV, and  $\pi-\pi^*$  satellite peak at 291.3 eV. Presence of C-O and C=O groups on the surface of the transferred PS colloidal array demonstrate an obvious change on the surface chemical structure and confirms UVO induced damage of the colloids due to over exposure.

### ***S9.0 Reflectance plot of transferred array***

Along with transmittance, we also looked into the reflectance spectra of samples with the NCP and HCP colloids transferred onto glass substrate, as shown in Fig. S3. The average reflectance of bare glass is  $\sim 4.5\%$  in the visible and IR spectral region (plot iii, Fig. S3). It reduced to  $\sim 2.1\%$  for a substrate containing transferred NCP array of 100 nm colloids (plot i). There is significant reduction in the % reflectance with NCP arrays of colloids of different diameters as well, when compared to respective with HCP arrays.



**Fig. S7** Reflectance spectra for transfer printed HCP and NCP arrays of PS colloids of diameters 100, 300 and 600 nm with respect to glass substrate. Inset shows the AFM image of transferred 100 nm NCP array formed using a grating template with  $I_P = 300$  nm.

#### References:

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